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(54) High Temperature Chemical Cement

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HIGH TEMPERATURE CHEMICAL CEMENT

ABSTRACT

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A high temperature chemical cement composition comprising temperature resistant particulate matter, a polymerizable resin capable of setting and maintaining its set under formation conditions, a liquid carrier, and a
10 foaming system comprising surfactant and air is disclosed. In its foamed condition the composition acts and performs as a fluid. Under formation conditions the resin will set and consolidate the composition into a rigid dense mass.

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HIGH TEMPERATURE CHEMICAL CEMENT

This invention relates generally to cements capable of use in oil and gas wells, and more particularly to high temperature cements capable of use in treating high temperature wells and other high temperature subsurface formations.

Cements used in oil and gas wells serve a variety of functions. Typically, oil and gas wells are walled with steel tubing called the casing. Cements are employed to secure the casing to the wall of the borehole usually by pumping the cement down the inside and up the outside of the casing to the desired level. Once the cement sets, the cement and casing provide a seal which protects surrounding fresh water resevoirs and the like from contamination by the formation fluids. Additionally, the cemented casing aids in supporting unconsolidated rock formations surrounding the borehole, and helps to prevent blowouts and subsequent waste of the reservoir's resources. Another important application of cement in oil and gas wells is its use in water-exclusion methods. In many oil and gas wells, the production of water makes the well uneconomical to operate. This can be overcome by placing a cement seal at the water-oil interface in a borehole to exclude water from the oil production.



Typical cements used in the above applications are cements of the portland and portland-pozzolan types. These cements are generally produced by burning a mixture of finely divided calcareous and argillaceous material and grinding the resultant residue to produce a fine powder. The calcium silicates and calcium aluminates produced by the calcining process react chemically with water to form a stone-like mass.

10 However, these types of cement are often inadequate when used in the high temperature, high pressure, corrosive environment of many deep wells and subsurface formations such as oil wells, hydrothermal wells, and other geothermal formations. Portland and pozzolan type cements
15 tend to deteriorate under these conditions often causing failure of the cemented well or formation.

Past methods of modifying portland type cements have proved unsatisfactory for many applications. Magnesium or
20 magnesium containing compounds have been added to portland cement to increase temperature resistance. Unfortunately, unpredictable swelling often occurs making the set of the cement unsatisfactory. In addition, the high viscosity of the magnesium containing slurry inhibits satisfactory
25 pumping in many instances. Addition of more water to improve pumpability further decreases the setting, curing and other physical qualities of the cement. Temperature resistance is claimed to be improved by the use of calcined serpentine, silica and a calcium silicate to form
30 a high temperature cement which is pumped into a well and allowed to hydrothermally cure to form a crystallized diopside and/or serpentine-containing phase. In addition, asbestos fibers have been added to portland type cements to improve temperature resistance, but the requirement of
35 a high water to asbestos ratio permits only the use of small amounts of asbestos fibers in order to maintain

adequate pumpability. In addition, too high an asbestos fiber content (generally greater than 2%) in the cement decreases the compressive strength of the cement.

5 In addition to difficulties with temperature resistance, stability and pumpability, setting time is a major disadvantage of portland type cement. The high temperature formations tend to decrease the set time significantly and impair pumpability. Retarder additives such as
10 calcium lignosulfonate and carboxymethyl hydroxyethyl cellulose have been added to portland cement to increase the setting time. Unfortunately, the results are generally unpredictable due to the absence of a homogeneous mixture of the additive throughout the cement. Improvements
15 have been provided for this condition by coating the cement grains with crosslinked hydroxyalkyl cellulose in an attempt to provide a uniform concentration of retarder throughout the cement.

20 Although improved portland type cements are available, a high temperature cement having overall qualities of high temperature resistance, stability, pumpability, chemical resistance and controllable setting time is desired.

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The present invention comprises a unique foamed high temperature chemical cement having the qualities of high strength, chemical resistance, controllable setting time, pumpability and stability.

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More particularly, the invention in one aspect pertains to a high temperature chemical cement composition comprising finely divided particulate cementing matter capable of use under high temperature conditions, a
35 polymerizable resin capable of coating the particulate

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matter and of setting and maintaining its set under the high temperature conditions, a liquid carrier, and a foaming agent capable of foaming the composition comprising air and surfactant.

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In its foamed condition, the composition is liquid in form or liquescent in that it can act and perform as a liquid, thus providing pumpability. At the subsurface formation temperature, the resin will set and consolidate the composition into a rigid dense mass.

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Accordingly, the invention also comprehends a method of cementing a subsurface zone comprising introducing the composition into a subsurface zone and maintaining the composition in the subsurface area until the resin has set. A polymer profile control treatment would further include introducing a polymer suitable for profile control into the fracture containing the cement matrix.

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Advantageously, the permeability of the set composition can be adjusted so as to provide a maximum barrier to the flow of oil, gas, steam, water and the like, or to provide a more permeable partial barrier. Partial barriers are desirable in forming a matrix for later polymer treatment of naturally fractured reservoirs having extremely high local permeability which generally prohibit traditional polymer profile control treatments. The permeability of the set composition can be adjusted by varying the amount of air and surfactant incorporated into the composition.

In addition, the setting time of the composition can be predetermined by varying the pH of the composition. Once set, the composition is stable to at least temperatures of about 400°F. Further, the composition once set is chemically resistant to hydrocarbons, acids, bases and most other non-oxidizing chemicals.

The subject invention is a novel high temperature chemical cement. The composition of the chemical cement comprises appropriate temperature resistant finely divided particles combined with a polymerizable resin capable of setting under formation conditions and maintaining its set, a liquid carrier, and a foaming system comprising surfactant and air. The foaming system provides a pumpable mixture of uniform concentration. Under formation conditions the resin sets, consolidating the composition into a rigid dense mass having high strength, temperature and chemical resistance and stability.

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The Particulate Matter Component

The particulate matter component of the compositions of this invention may be any suitable finely divided particulate cementing matter, such as powders, dusts, or flours such as silica flour, capable of use under high temperature formation conditions which have the capability of forming a highly impermeable mass in conjunction with a set resin. In addition, the particulate matter is chosen for its strength, economy, and compatibility with other components of the composition and the formation fluids.

The Thermosetting Resin

Various resins may be used in the present invention. This includes true thermosetting resins, often referred to as one-step resins because no curing agent is required, and two-step thermosetting resins which utilize a catalyst for curing. An example of a true thermosetting resin would be a phenolic, or phenol-formaldehyde, resin of the resole type. An example of a two-step resin would be a phenolic resin of the novolac type. Other thermosetting resins of the aminoplast type may also be used, including urea-formaldehyde and melamine-formaldehyde resins.

Although these resins may be used as one-step resins, addition of acid catalysts will speed the curing time.

Furan resins, including resins produced from the reaction of furfuryl alcohol with urea, formaldehyde or phenols, may also be used. These resins are generally cured by addition of mineral or organic acid catalysts, although occasionally alkaline catalysts are used for curing. In addition, it is contemplated that epoxy type resins may also be used.

In a preferred embodiment of the present invention, an oil-soluble resin is desirable, for example a urea-

formaldehyde resin. This allows addition of substantial amounts of water without affecting the polymerization of the resin.

5 Of primary importance in choosing a resin is the ability to control the setting time. A sufficient amount of time must be allowed for preparation of the composition, storage, and introduction of the mixture into the subsurface formation before setting. In this respect, an
10 oligomer type resin is preferred to a monomer type resin because of the increased setting time for the oligomer.

 If the thermosetting resin is of the two-step variety, a catalyst is generally required. Acid catalysts are
15 usually employed, although base catalysis is generally employed in limestone formations. Generally as the pH of the composition is decreased by addition of the acid catalyst, a corresponding decrease in resin setting time results. In a preferred embodiment of the invention, a
20 buffered acid catalyst is used to raise the pH of the composition, thereby increasing the setting time of the resin while leaving the total acid quantity nearly the same.

25 If desired, the resin may be pre-coated on the particulate matter before combining it with the other components of the composition. Methods for making resin coated particles are well known in the art, as typified by Nesbit et al., U.S. Patent No. 2,986,538. Pre-coating is deemed
30 especially desirable in those instances where the resin-forming material is soluble in water and the liquid carrier is water.

The Liquid Carrier

Any suitable liquid may be used in practicing the present invention. In general, the liquid is chosen on the basis of its economy, fluidity, and chemical compatibility with the rock formation and the reservoir fluids. Water, brine and like liquids are generally preferred because they are economical.

10 The Foaming System

The components required to produce a foamed fluid in accordance with the present invention will normally include a surfactant and air foaming agent. The foaming agent helps maintain the liquidity of the overall composition. The surfactant may be cationic, anionic or non-ionic, but it must be capable of generating a foam with a liquid carrier and air at ambient temperatures. Examples of surfactants which may be used are soaps, synthetic detergents, and proteins. Desirable surfactants can be selected from the many alkyl aromatic sulfonic acids. A principal purpose of the surfactant is to control bubble life in the foam. Bubble strength can be increased by adding minute amounts of polyvalent cations which further stabilizes the foam.

The foaming system can be adapted to give a set cement with minimal permeability, such as desired for plugging a well or sealing a porous formation, or to give a set cement having more than minimal permeability, such as desired for providing a matrix for polymer profile control treatments. Generally, the fractures of naturally fractured resevoirs have extremely high local permeability, and as a result typical polymer profile control has limited success. By regulating the foaming system to provide a more permeable cement, an effective cement

matrix can be provided in the fracture so that a polymer will hold.

Generally, the foaming system can be adapted to
5 provide a cement with more than minimal permeability by
(1) incorporating more air into the composition, (2) in-
creasing the concentration of surfactant in the composi-
tion, or both. Cements of minimal permeability are pro-
vided by incorporating as little air as possible into the
10 composition and decreasing surfactant composition.

EXAMPLES

The following examples describe the invention in more
15 detail. Such examples are for the purpose of illustrating
the invention and do not limit the scope of the invention.

Example 1

20 A chemical cement for use under conditions where
minimal permeability is desired was constructed from the
components listed in Table 1.

TABLE 1

| | Material | Equivalent Field Units | Laboratory Weight | Comments |
|----|--------------------------------------|---------------------------|----------------------|--|
| 5 | Silica Flour | 208 lb. | 500 g | 400 mesh |
| | Resin I | 1.70 gal. | 40 g | Urea/formaldehyde type |
| 10 | Resin II | 1.76 gal. | 40 g | Quacorr [*] 1300: Butyl Acetate (80:20 by wt.) |
| 15 | Catalyst Component | 2.10 gal. | 50 g | 39.2% Phosphoric Acid (85%), 4.4% Fluosilicic Acid (40%), 20.0% Toluene Sulfonic Acid, 36.4% Water |
| 20 | Surfactant- Catalyst Component | 3.80 gal. | 100 g | 35.3% Phosphoric Acid, 3.9% Fluosilicic Acid, 18% Toluene Sulfonic Acid, 10% Dodecyl Benzene Sulfonic Acid, 32.8% Water |
| 25 | | | | |
| | Water/Ammonium Hydroxide | 10.00 gal. | 200 g | Enough Ammonium Hydroxide to bring the mixture's pH to 6 |
| 30 | | | | |

The Quacorr^{*} 1300 referred to in Table 1 is a partially
polymerized furfuryl alcohol resin supplied by the Quaker Oats
Chemical Company (the butylacetate serves as a solvent for the resin)
35 as well as a water scavenger for the polymerization reaction.)

Example 2

40 The components of Example 1 were mixed in a Kitchen
Aide^{*} mixer at the lowest speed setting so as to incorpo-
rate as little air as possible. The silica flour was
mixed with resins I and II until coated. The catalyst and
surfactant components and the water/ammonium hydroxide
45 solution were then added. (These may be premixed before
adding). Mixing was continued until the silica flour

* Trademarks

mixture was liquidized. Further mixing will not damage the results.

Example 3

5

A six inch pipe nipple was packed with solvent stripped formation material and equipped with fittings. An initial permeability to water was measured and found to be 3.49 darcies. A liquidized silica flour mixture prepared according to Example 2 was injected into the pipe nipple under 5 psi and allowed to set. The core was then uncapped and visually inspected. The silica flour was well dispersed in the core as evidenced by the uniform consolidation of the core material at both injection and production ends of the core. The core was recapped with clean end caps and the permeability was remeasured. The core was found to be plugged. The core was then placed in an oven at 392°F for 96 hours to see if the heat would degrade the polymerized resin. After the 96 hours, the permeability was remeasured and the core was found to still be plugged. Visual examination revealed no damage as well.

Example 4

25

A chemical cement for use under conditions where more than minimal permeability is desired was constructed from the components listed in Table 2.

TABLE 2

| | Material | Equivalent Field Units | Laboratory Weight | Comments |
|----|--------------------------------------|---------------------------|----------------------|---|
| 5 | Silica Flour | 208 lb. | 500 g | 400 mesh |
| | Resin I | 1.70 gal. | 40 g | Urea/formaldehyde type |
| 10 | Resin II | 1.76 gal. | 40 g | Quacorr 1300: Butyl Acetate (80:20 by wt.) |
| | Catalyst Component | | None | |
| 15 | Surfactant- Catalyst Component | 5.7 gal. | 150 g | Increased amount of the surfactant component as described in Table 1. |
| 20 | | | | This component contains 0.5% Aluminum cation based on the Dodecyl Benzene Sulfonic Acid weight. |
| 25 | Water/Ammonium Hydroxide | 10.0 gal. | 200 g | Enough Ammonium to bring the pH to 6. |

30 Example 5

The components of Example 4 were mixed as in Example 2 with the exception that more air was incorporated into the mixture to produce a more highly foamed composition.

35 As evidenced in Table 2, foaming was further increased by adding more surfactant. The soap bubbles of the foam were strengthened by use of an aluminium cation as a foam stabilizer.

40 Example 6

A fracture-like environment was created for testing the compositions of Examples 1 and 4 in the following manner. Two Berea cores, 2x2x12 inches were cut in half
45 and two grooves were placed on each of the newly formed

faces. The cores were then fitted back together according to their original orientation with the sides of the cores sealed with epoxy. The grooves served to insure a fracture-like environment within the cores. The cores
5 were then equipped with fittings at each end to facilitate the introduction of fluids and cast in epoxy resin. After the epoxy resin had set, the cores were ready for treatment.

10 Example 7

An initial permeability to water was run on one of the cores prepared according to Example 6 and found to be 14.67 darcies. Liquidized silica flour constructed
15 according to Example 2 was gravity flowed into the core and allowed sufficient time to set. The permeability was remeasured and found to be 0. The fittings were removed and found to be plugged. The core was fitted with new fittings and the permeability was found to be 0.822
20 darcies. This corresponds to a 94.4% reduction in permeability.

Example 8

25 An initial permeability to water was run on the other ~~core prepared in accordance with example 6 and was found~~
to be 21.7 darcies. Liquidized silica flour prepared according to Example 5 was gravity flowed into the core. After the silica flour had set and the fittings were
30 replaced, the permeability was remeasured and found to be 1.64 darcies. This corresponds to a 92.4% reduction in permeability. A summary of the results are listed below in Table 3.

TABLE 3
FRACTURE RESULTS

| 5 | <u>Example</u> | <u>Initial K</u> | <u>Final K</u> | <u>% Reduction</u> |
|----|----------------|------------------|----------------|--------------------|
| | 7 | 14.67 darcies | 0.82 darcies | 94.4 |
| 10 | 8 | 21.70 darcies | 1.64 darcies | 92.4 |

Because the mixture is non-viscous and the aggregate used, the silica flour, is very fine (400 mesh), the mixture will penetrate high permeability formations easily.

15

In the practice of the invention, the rate of polymerization of the resin material generally increases along with increasing temperature. In addition, polymerization rate is varied by the type of resin used. A monomer-type resin will polymerize faster than an oligomer-type resin, given the same monomer chemistry. The Quacorr 1300 referred to in the above examples is water-insoluble. Since Quacorr 1300 is an oligomer, it polymerizes slowly, and since it is oil-soluble, it permits substantial amounts of water to be added to the mixture thereby increasing liquidity but not suppressing the setting polymerization reaction.

In the compositions describe above, changing the quantity of acid downward to extend setting time could prevent polymerization entirely. Adding 6N ammonium hydroxide to the acid mixture to raise the pH had the effect of leaving the total acid quantity nearly the same while providing hydrogen ions more slowly. The higher the pH, the longer the set time for a given temperature. Consequently, higher temperature mixtures require a higher pH to achieve the same set time as lower temperature mixtures. Very high temperatures may require reduction of total acidity.

The foregoing description has been directed to a particular embodiment of the invention for the purposes of illustration and explanation. Those skilled in the art will readily appreciate modifications and changes in the
5 procedures and components set forth without departing from the scope and spirit of the invention. Applicant's intent is that the following claims be interpreted to embrace all such modifications and variations.

The Embodiments of the Invention in which an Exclusive Property or Privilege is claimed are defined as follows:

1. A high temperature chemical cement composition
5 comprising:

- (a) finely divided particulate cementing matter
capable of use under high temperature
conditions;
10
- (b) a polymerizable resin capable of coating said
particulate matter and of setting and maintain-
ing its set under said high temperature
conditions;
15
- (c) a liquid carrier;
- (d) a foaming agent capable of foaming said composi-
tion comprising air and surfactant.
20

2. The composition of claim 1 in which the particulate
matter is silica flour.

25 3. The composition of claim 1 in which the resin is a
thermosetting resin.

30 4. The composition of claim 1 in which the resin is a
two-step catalyzed resin.

5. The composition of claim 1 in which the resin is a
35 partially polymerized furfuryl alcohol.

6. The composition of claim 1 in which the liquid carrier is water or brine.

5 7. The composition of claim 1 in which the foaming system further comprises entrained air.

8. The composition of claim 1 in which the surfactant is
10 an alkyl aromatic sulfonic acid.

9. The composition of claim 1 further comprising a foam stabilizer.
15

10. The composition of claim 1 further comprising a catalyst to catalyze the polymerization of said resin.

20 11. A method of polymer profile control treatment comprising:

25 A. introducing into a fracture a composition capable of providing a permeable cement matrix comprising:

(1) particulate cementing matter capable of use in subsurface formation fractures;

30 (2) a polymerizable resin capable of coating said particulate matter and of setting and maintaining its set under formation conditions;

35

(3) a liquid carrier; and

(4) a foaming agent capable of foaming said
composition comprising surfactant and air;

5

B. maintaining said composition in said fracture
until the resin has set; and

10 C. introducing a polymer suitable for profile
control into said fracture containing said
cement matrix.

12. The method of claim 11 in which the particulate
15 matter is silica flour.

13. The method of claim 11 in which the resin is a
thermosetting resin.

20

14. The method of claim 11 in which the resin is a two-
step catalyzed resin.

25

15. The method of claim 11 in which the resin is a
partially polymerized furfuryl alcohol.

30 16. The method of claim 11 in which the liquid carrier is
water or brine.

17. The method of claim 11 in which the air is entrained
35 into the composition.

18. The method of claim 11 in which the surfactant is an alkyl aromatic sulfonic acid.

5 19. The method of claim 11 which includes adding a foam stabilizer to the composition.

20. The method of claim 11 which includes adding a
10 catalyst to the composition to catalyze the polymerization of said resin.

21. A method of cementing a subsurface zone comprising:
15

A. introducing into a subsurface zone a composition comprising:

(1) particulate cementing matter capable of use
20 under subsurface conditions;

(2) a polymerizable resin capable of coating
said particulate matter and of setting and
maintaining its set under subsurface
25 conditions;

(3) a liquid carrier; and

(4) a foaming agent capable of foaming said
30 composition comprising surfactant and air;
and

B. maintaining said composition in said subsurface
area until said resin has set.
35

22. The method of claim 21 in which the particulate matter is silica flour.

5 23. The method of claim 21 in which the resin is a thermosetting resin.

24. The method of claim 21 in which the resin is a two-
10 step catalyzed resin.

25. The method of claim 21 in which the resin is a partially polymerized furfuryl alcohol.
15

26. The method of claim 21 in which the liquid carrier is water or brine.

20 27. The method of claim 21 in which the air is entrained into the composition.

25 28. The method of claim 21 in which the surfactant is an alkyl aromatic sulfonic acid.

29. The method of claim 21 which includes adding a foam
30 stabilizer to the composition.

30. The method of claim 21 which includes adding a catalyst to the composition to catalyze the polymerization
35 of said resin.



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